



# Pyrolysis of coal, biomass and their blends: Performance assessment by thermogravimetric analysis



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## HIGHLIGHTS

- Coal and biomass pyrolysis has been studied via thermogravimetric analysis (TGA).
- South African coal, Sardinian Sulcis coal and wood chips have been characterized.
- S. African coal thermal decomposition is very low, thus indicating a low reactivity.
- Coal and biomass do not show sensible synergic effects when they are co-pyrolyzed.
- Pyrolysis behavior through TGA allows to optimize the pilot-scale gasification.

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## ABSTRACT

With the aim to support the experimental tests in a gasification pilot plant, the thermal decomposition of coal, biomass and their mixtures has been carried out through a thermogravimetric analysis (TGA) and a simplified kinetic analysis. The TGA of pure fuels indicates the low reactivity of South African coal and the relatively high reactivity of Sardinian Sulcis coal during pyrolysis. Among the tested fuels, biomass (stone pine wood chips) is the most reactive one. These results fully confirm those obtained during the experimental tests in the gasification pilot plant. As for the fuel blends, the analysis shows that the synergic effects between the considered coals and biomass are negligible when they are co-pyrolyzed. The results of the analysis confirm that TGA could be very useful to generally predict the gasification performance and to optimize the experimental campaigns in pilot-scale gasification plants.

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## 1. Introduction

Coal and biomass are the first and the third largest energy resources in the world (the second being oil), respectively (Chen et al., 2012). A sustainable energy production will need, for several decades, the use of fossil fuels (coal in particular) as primary sources for power generation (Lucquiaud and Gibbins, 2011). But the combustion of fossil fuels represents the main contribution to anthropogenic CO<sub>2</sub> emissions (Lohwasser and Madlener, 2012; Huang et al., 2008). The increasing attention to climate changes is leading to the growing interest on renewable sources and carbon capture and storage (CCS) technologies (Varol et al., 2010). This justifies the candidacy of biomass as supplementary source for meeting part of the world's energy demand (Varol et al., 2010).

The knowledge of the thermal decomposition of coal and biomass is essential to assess the performance of carbonization,

combustion and gasification processes (Seo et al., 2011). In particular, the pyrolysis processes can be considered as the initial stage of thermal conversion processes of carbonaceous materials, including combustion and gasification. So, an improved understanding of coal and biomass pyrolysis can be used to predict the process performance in a gasification reactor. Therefore, several studies have been recently published on pyrolysis of different fuels, mainly coal and biomass. Thermogravimetric analysis (TGA) is the simplest and the most effective technique to observe both the pyrolysis and combustion profiles of a fuel (Varol et al., 2010). Pyrolysis behavior is typically assessed by performing the analysis in an inert (nitrogen or argon) atmosphere, whereas combustion profile is determined by feeding the thermogravimeter with an oxidant gas (usually air).

Shi et al. (2013) compare the pyrolysis performance of 34 different Chinese coals, from lignite to anthracite. A Chinese coal (from Shin-Wha) is also studied by Seo et al. (2011) by using a thermogravimeter and a lab-scale furnace. Several studies also refer the TGA results of mixtures of coal and biomass: Park et al. (2010) present the results of coal and sawdust blend in thermogravimeter

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**Table 1**  
Brief summary of recent literature review.

Source	Fuel type	Max. temp. (°C)	Heating rate (°C/min)	Sample wt.	Atmosph.
Shi et al. (2013)	34 Different Chinese coals, from lignite to anthracite	900	10	30 mg	Ar
Seo et al. (2011)	Chinese (Shin-Wha) coal	900	5, 10, 20, 30	0.8 g	N <sub>2</sub>
Park et al. (2010)	Sawdust ( <i>Larix leptolepsis</i> ) and sub-bituminous coal	700	30	10 mg	N <sub>2</sub>
Chen et al. (2012)	Microalgae ( <i>Chlorella vulgaris</i> ) and Chinese semi-anthracite	1000	10, 20, 40	6 mg	N <sub>2</sub>
Idris et al. (2010)	Mukah Balingian (Malaysian) low rank coal and oil palm	900	10, 20, 40, 60	10 mg	N <sub>2</sub>
Lu et al. (2013)	Torrefied wood ( <i>Cryptomeria japonica</i> ) and anthracite	800	20	5 mg	N <sub>2</sub>
Ceylan and Topçu, (2014)	Hazelnut husk from Turkey	1000	5, 10, 50	10 mg	N <sub>2</sub>
Kumar et al. (2008)	Corn stover ( <i>Zea mays</i> ) from Nebraska, USA	850	10, 30, 50	5–10 mg	N <sub>2</sub>
Sait et al. (2012)	Date palm ( <i>Phoenix dactylifera</i> ) from Saudi Arabia	900	20	5 mg	N <sub>2</sub>
Syed et al. (2011)	Jordanian oil shale	800	5, 10, 15, 20	8–15 g	N <sub>2</sub>
Park et al. (2012)	Korean refuse plastic fuel	800	10, 20, 30, 40	1.0–1.5 g	N <sub>2</sub>
Quan et al. (2013)	Hazardous material contained in electronic equipment	700	10	10 mg	N <sub>2</sub>

and fixed-bed reactor, whereas Chen et al. (2012) consider a mixture of coal and an unicellular green microalgae. Idris et al. (2010, 2012) investigate through TGA the behavior of different blends of Malaysian coal and oil palm for both pyrolysis and combustion processes. Lu et al. (2013) investigate the co-pyrolysis of torrefied wood and Australian anthracite. Several other interesting studies, specifically referred to biomass and wastes pyrolysis (and frequently also combustion), can be found in the literature. Ceylan and Topçu (2014) present the kinetic analysis of hazelnut husk pyrolysis, Kumar et al. (2008) characterize North American corn stover from the kinetic point of view, Sait et al. (2012) present a similar analysis, referred to date palm from Saudi Arabia, whereas samples of oil shale are analyzed by Syed et al. (2011). As for wastes, refuse plastic fuel is characterized by Park et al. (2012), whereas electronic waste is tested by Quan et al. (2013).

These studies typically differ not only in terms of fuels, but also as for samples preparation and analytical methodology. A brief review of several interesting studies on pyrolysis by TGA is reported in Table 1.

Sotacarbo is engaged in a series of coal and biomass gasification experimental campaigns in a pilot plant, based on a fixed-bed gasifier (Pettinau et al., 2014b, 2011). As obvious, fuel's thermochemical properties strongly condition the gasification performance and their evaluation through a TGA method could allow to optimize the experimental tests on the pilot unit.

This paper reports the main results of a pyrolysis performance assessment of three of the most representative fuels tested in the Sotacarbo plant and their mixtures. In particular, the following fuels have been analyzed: (i) a low reactive South African bituminous coal (SAF), (ii) a high reactive local sub-bituminous Sulcis coal (SUL), characterized by a very high sulfur content, (iii) a local biomass (stone pine wood chips, WCH) and (iv) several mixtures of the above mentioned fuels.

## 2. Methods

The three considered fuels have been selected being representative of different behavior during more than 2200 h of gasification tests (since 2008) in the Sotacarbo plant. Then they have been characterized according to the methods described below.

### 2.1. Summary of pilot-scale gasification performance

The Sotacarbo pilot plant is based on a fixed-bed up-draft gasifier, operating at atmospheric pressure and characterized by an internal diameter of 300 mm and a total height of 2000 mm. The reactor is fed with coal and/or biomass, with a particle size of 5–15 mm, periodically loaded through the top of the gasifier to maintain constant (at about 1000–1200 mm) the fuel bed level, supported by a grate which also allows the discharging of bottom ash.

Gasification agents (air and steam, both pre-heated up to 250 °C) are injected through the grate; they flow upward through the reactor, allowing the different processes that commonly occur in this kind of process: ash cooling, combustion and gasification, pyrolysis, drying and devolatilization, respectively (Hobbs et al., 1992).

A more detailed description of the Sotacarbo pilot plant and the experimental procedures can be found in previous papers (Pettinau et al., 2014a,b).

Table 2 summarizes the average gasification performance of the three considered fuels, here reported to compare the results with those of the TGA.

Among the other parameters, Table 2 reports the specific gasification rate (SGR, expressed in kg/m<sup>2</sup> h), defined as the amount of gasified fuel (kg/h) divided by the area (m<sup>2</sup>) of the horizontal section of the fuel bed. It can be used as representative parameter of the fuel reactivity. For fixed-bed gasifiers, SGR corresponds to the so-called grate loading (GL), defined as the amount of fuel gasified per square meter of grate area.

As results from the pilot-scale experimental tests, South African bituminous coal is characterized by a low reactivity (with a specific gasification rate of 113.2 kg/m<sup>2</sup> h), and its gasification in fixed-bed

**Table 2**  
Typical gasification conditions and performance.

	S. African coal	Sulcis coal	Stone pine wood chips
<i>Operating parameters</i>			
Fuel consumption (kg/h)	8.0	9.2	12.0
Air mass flow (kg/h)	36.8	39.2	11.3
Steam mass flow (kg/h)	3.7	2.5	0.0
<i>Raw syngas composition (molar fractions, dry basis)</i>			
CO	0.1807	0.1583	0.2207
CO <sub>2</sub>	0.0947	0.0948	0.0797
H <sub>2</sub>	0.1889	0.1200	0.3342
N <sub>2</sub>	0.5128	0.5606	0.3418
CH <sub>4</sub>	0.0151	0.0236	0.0119
H <sub>2</sub> S	0.0003	0.0121	0.0000
COS	0.0001	0.0019	0.0000
O <sub>2</sub>	0.0074	0.0233	0.0117
Other (C <sub>2</sub> H <sub>6</sub> and C <sub>3</sub> H <sub>8</sub> )	0.0000	0.0054	0.0000
<i>Raw syngas properties (dry basis)</i>			
Mass flow (kg/h)	46.83	48.91	23.31
Volume flow (Nm <sup>3</sup> /h)	42.90	41.55	25.48
Lower heating value (MJ/kg)	4.50	3.59	7.49
Specific heat (kJ/kg K)	1.23	1.14	1.47
Outlet pressure (MPa)	0.14	0.14	0.14
<i>Main gasifier performance indicators</i>			
Maximum temp. (°C)	1034	950	730
Cold gas efficiency	96.93%	90.60%	84.33%
Gasifier yield (Nm <sup>3</sup> /kg)	5.36	4.52	2.12
SGR-GL (kg/m <sup>2</sup> h)	113.2	130.1	169.8

reactors operating at atmospheric pressure involves a high content of residual carbon in the discharged ash. On the contrary, the local high sulfur sub-bituminous coal (from the Sulcis coal mine, located in South-West Sardinia, Italy, about 20 km far from the Sotacarbo Research Centre and pilot plant) presents a very high reactivity (SGR of 130.1 kg/m<sup>2</sup> h), allowing the production of a high syngas flow. But raw syngas is characterized by a high sulfur content, which requires a very efficient desulfurization system. Moreover, high volatile and moisture content of Sulcis coal involves relatively low gasification temperatures, with a subsequent high tar production. Finally, stone pine (*Pinus pinea*) wood chips (from local forests) present a relatively high reactivity (SGR of 169.8 kg/m<sup>2</sup> h) and it could be a supplementary fuel to be mixed with both Sulcis coal (in order to reduce the sulfur content in the blend) and South African coal (in order to improve the fuel reactivity).

## 2.2. Samples preparation

In most of the thermogravimetric studies reported in the literature, samples are previously dried in order to make different fuels comparable by removing a variable, the moisture content, which is not only an intrinsic fuel property (it depends on the history of the fuel sample). On the other hand, commercial gasification plants are usually fed with fuels with their original moisture content. Several preliminary tests have been carried out to compare the pyrolysis behavior of dry and as received (AR) samples (the latter stored for at least seven days into the laboratory, with a relative air humidity of about 60%, in order to make the surface moisture uniform). The analysis show that the pyrolysis behavior of the AR samples differs from the corresponding one of the dry samples only during the first phase of the heating process, up to about 100–105 °C. Therefore, the results here presented, referred to the dry samples, can be considered representative of the behavior of the fuel during a commercial scale process.

Each sample has been crashed into a cross beater mill (Retsch SK100) and sieved in order to obtain a particle size lower than 125 µm. A portion of the resulting material is used as “as received” samples (used for the preliminary analyses and for the general characterization in terms of proximate, ultimate and thermal analyses), whereas the remaining is dried into an oven with a constant temperature of 105 ± 2 °C for at least 24 h and then stored in desiccators to prevent moisture absorption from atmosphere (Park et al., 2010; Chen et al., 2012).

As for the fuel blends, each sample has been thoroughly mixed and homogenized before the analysis (Varol et al., 2010).

## 2.3. Proximate, ultimate and thermal analysis

Both dry and “as received” samples of each fuel, prepared according to the previously described procedure, have been characterized through the conventional proximate, ultimate and thermal analyses, which results are reported in Table 3. Proximate analysis is performed by a thermogravimeter LECO TGA-701 (based on the ASTM D 5142-04 “Moisture Volatile Ash” standard); ultimate analysis is obtained by a LECO Truspec CHN/S analyzer (based on ASTM D 5373-02 for carbon, hydrogen and nitrogen and ASTM D 4239-05 for sulfur); finally, higher heating values are measured by a LECO AC-500 calorimeter according to the standard ISO 1928:1995.

All the analyses reported below have been carried out in the Sotacarbo Laboratories in Carbonia, Italy.

## 2.4. Experimental apparatus and test procedures

The characterization of the considered samples by TGA has been carried out by using the same LECO TGA-701 thermogravimeter used for the fuels' proximate analysis. Each sample (characterized by a mass of 1 ± 0.05 g) has been loaded into a ceramic crucible and placed into the thermogravimeter.

During the test, each sample has been heated into the thermogravimeter according to the following steps: (i) heating from ambient temperature (about 30 °C) to 105 °C at a constant rate of 10 °C/min; (ii) temperature is maintained constant for 10 min in order to assure a complete removal of free-water (Chen et al., 2012); (iii) heating up to 1000 °C (Chen et al., 2012; Ceylan and Topçu, 2014) at different constant rates, typically 10, 20, 30 and 40 °C/min (Chen et al., 2012; Idris et al., 2010, 2012); (iv) temperature is maintained constant at 1000 °C for other 10 min, in order to eventually complete the pyrolysis process; (v) cooling of the instrument to ambient temperature. During all the tests, a constant nitrogen flow (3.5 dm<sup>3</sup>/min, with a purity of 99.99945% by volume) is sent to the thermogravimeter to ensure an inert atmosphere. Each test has been performed two times, in order to assure the complete repeatability of the analysis.

## 2.5. Kinetic analysis

The kinetic parameters could be calculated through TGA without considering complex chemical reactions during thermal decomposition process, which is an important and difficult task in many thermal applications (Gu et al., 2014).

**Table 3**  
Primary fuels characterization.

	S. African dry	S. African AR	Sulcis dry	Sulcis AR	Wood ch. dry	Wood ch. AR
<i>Proximate analysis (% by weight)</i>						
Fixed carbon <sup>a</sup>	77.51	72.06	42.55	34.22	19.01	17.69
Volatiles	14.38	9.09	43.27	41.22	78.26	73.31
Moisture	0.00	2.28	0.00	4.70	2.74	8.57
Ash	8.11	16.57	14.18	19.86	0.90	0.43
<i>Ultimate analysis (% by weight)</i>						
Total carbon	85.88	74.50	63.22	55.85	56.03	49.10
Hydrogen	2.84	2.66	4.43	4.65	6.02	6.20
Nitrogen	1.50	1.39	1.59	1.48	0.07	0.01
Sulfur	0.56	0.48	7.14	6.63	0.00	0.00
Oxygen <sup>a</sup>	1.11	2.12	9.44	6.83	34.24	35.69
Moisture	0.00	2.28	0.00	4.70	2.74	8.57
Ash	8.11	16.57	14.18	19.86	0.90	0.43
<i>Thermal analysis (MJ/kg)</i>						
HHV	31.77	28.10	25.31	22.59	20.03	19.23

<sup>a</sup> By difference.

In general, when a solid-state reaction is carried out in non-iso-thermal conditions (and, in particular, under a linear temperature program), the sample mass can be measured as a function of temperature (Shuping et al., 2010). The rate of conversion,  $d\alpha/dt$ , can be expressed as (Chen et al., 2012):

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where  $\alpha$  is the conversion degree,  $t$  is time (in s),  $T$  is the absolute temperature (in K),  $k(T)$  is a temperature-dependent rate constant and  $f(\alpha)$  is a function related with the reaction mechanism. In particular, the conversion degree can be defined as (Xiao et al., 2009; Zuru et al., 2004):

$$\alpha = \frac{m_i - m_t}{m_i - m_\infty} \quad (2)$$

where  $m_i$  is the initial mass of the sample,  $m_t$  is the mass at time  $t$  and  $m_\infty$  is the mass of the sample at the end of the test (all expressed in g).

The constant  $k(T)$  can be defined, according to the Arrhenius equation, as (Chen et al., 2012; Shuping et al., 2010):

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (3)$$

where  $A$  is the pre-exponential factor (1/s),  $E$  is the activation energy (J/mol) and  $R$  is the universal gas constant (J/mol K).

As mentioned above, the sample heating rate during the analysis has been maintained constant (typically at 10, 20, 30 or 40 °C/min). Therefore, it is possible to define the variation of  $\alpha$  with the temperature instead of the time. In particular, the combination of Eqs. (1) and (3) gives:

$$\frac{d\alpha}{dt} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) \cdot f(\alpha) \quad (4)$$

being  $\beta$  the heating rate (K/s), defined as:

$$\beta = \frac{dT}{dt} \quad (5)$$

An integration of Eq. (4) can be written as (Chen et al., 2012):

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \quad (6)$$

$$T = T_0 + \beta \cdot t \quad (7)$$

where  $T_0$  is the initial temperature (in K) of the experiment (Cai and Liu, 2008).

The kinetic parameters of the considered process can be analyzed by using different iso-conversional methods. In this study, the Flynn–Wall–Ozawa (FWO) method has been considered (Xiao et al., 2009; Shuping et al., 2010; Chen et al., 2012); it is an integral thermal analysis method which could be applied to determine the apparent activation energy of pyrolysis process at different heating rates (Gu et al., 2014). The FWO method can be expressed as (Shuping et al., 2010):

$$\ln \beta = \ln \frac{0.0048AE_\alpha}{Rg(\alpha)} - 1.0516 \frac{E_\alpha}{RT} \quad (8)$$

when  $\alpha$  is constant, the values of  $\ln \beta$  versus  $1/T$  (obtained at different values of the heating rate  $\beta$ ) can be correlated by a straight line, of which the slope indicates the activation energy  $E$  (Chen et al., 2012).

### 3. Results and discussion

The experimental results of the thermogravimetric analyses of the considered fuels and fuel blends are represented and compared by using the thermogravimetric (TG) profiles and the differential thermogravimetric (DTG) curves. Moreover, as mentioned above, the kinetic analysis, based on the experimental data processed through the previously described model, has been carried out to determine the activation energy of the pyrolysis process.

#### 3.1. TG and DTG profiles

TG profile shows the weight loss of the sample as a function of temperature (it represents the simple functional relationship of weight change), whereas DTG profile is the derivatives of TG curve, which peaks correspond to the inflexion points of a TG-curve: both these curves allow a precise mapping of the thermal processes within the sample (Pettinau et al., 2014a).

Fig. 1 shows the TG curves of the three considered fuels (Sulcis and South African coals and stone pine chips) at different heating rates.

As expected, apart from the heating rate, wood chips present a very high weight loss, mainly between 200 and 420 °C, due to its high reactivity; on the other hand, coal TG behavior is slower, in particular for the South African coal, which is characterized by a high content of inert material (ash) and a low volatile content. Fig. 1 also shows the effect of the heating rate on the TG behavior: the increasing of the heating rate shifts the thermal degradation profile toward the higher temperatures, delaying sample decomposition and involving a lower weight loss (Xiao et al., 2009; Park et al., 2012; Agarwall and Lattimer, 2014, as a consequence of the differences in heat transfer and kinetic rates (Seo et al., 2011; Shuping et al., 2010). A slight overlapping between the curves, mainly for the higher heating rates, can be noticed (Gu et al., 2014; Seo et al., 2011; Shuping et al., 2010) for wood chips. TG profiles of South African coal represent, among the considered fuels, an opposite behavior with respect to wood chips. Whereas in dry wood chips a significant weight loss can be observed at relatively low temperatures (200–420 °C), South African coal starts its weight reduction since about 450 °C.

The previous preliminary analysis suggests to assume the heating rate of 20 °C/min as the most representative one for the analysis here reported. This heating rate has been chosen to minimize systematic errors in temperature measurement due to thermal lag during pyrolysis (Masnadi et al., 2014). As a matter of facts, as anticipated, higher heating rates involve, mainly for biomass, an irregular weight reduction. Fig. 2 shows, for the three considered fuels and for their mixtures (at 50% by weight), the TD and DTG profiles, respectively.

As for the pure fuels, the analysis confirms the results of the pilot-scale gasification tests. The relatively low weight reduction (80% of the initial value, as shown in Fig. 2a) of South African coal indicates a low reactivity of such a fuel, which is consequence of the high carbon and low volatiles contents. This involves the low values of fuel consumption (8.0 kg/h) and specific gasification rate (113.2 kg/m<sup>2</sup> h) shown in Table 2. On the other hand, Sulcis coal is more reactive than South African one, presenting a higher weight reduction (56% of the initial value) during the TGA analysis and a SGR of 130.1 kg/m<sup>2</sup> h during the pilot-scale experimental tests. DTG curve (Fig. 2b) of Sulcis coal shows a devolatilization peak at 453 °C: this condition can be observed during pilot-scale gasification tests at a height of about 800–900 mm from the grate. As for wood chips gasification, the high fuel reactivity shown by both TG and DTG profiles (with an overall weight reduction to about 10% of the initial value) is fully confirmed by the pilot-scale experimental

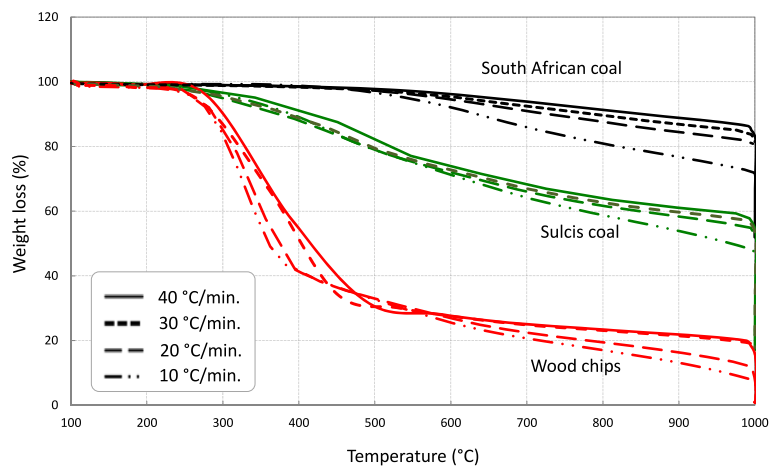


Fig. 1. TG profiles for the three considered fuels at different heating rates.

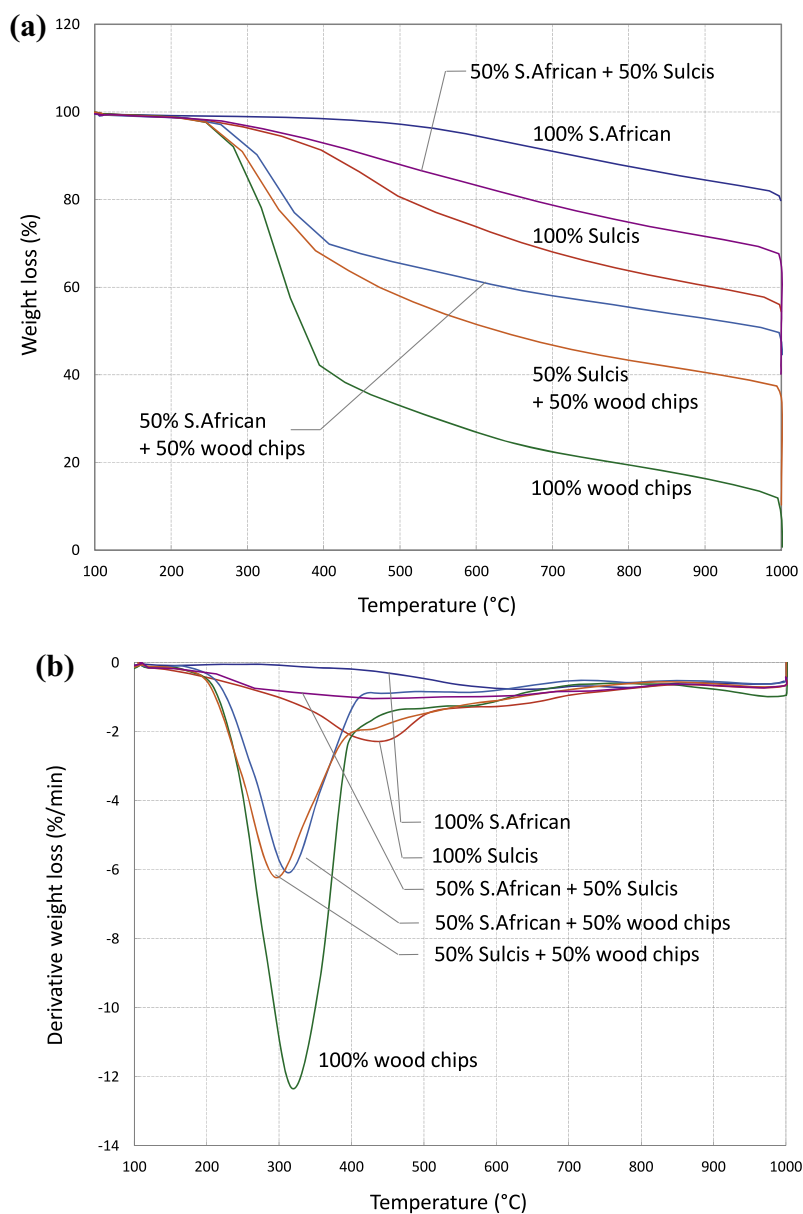
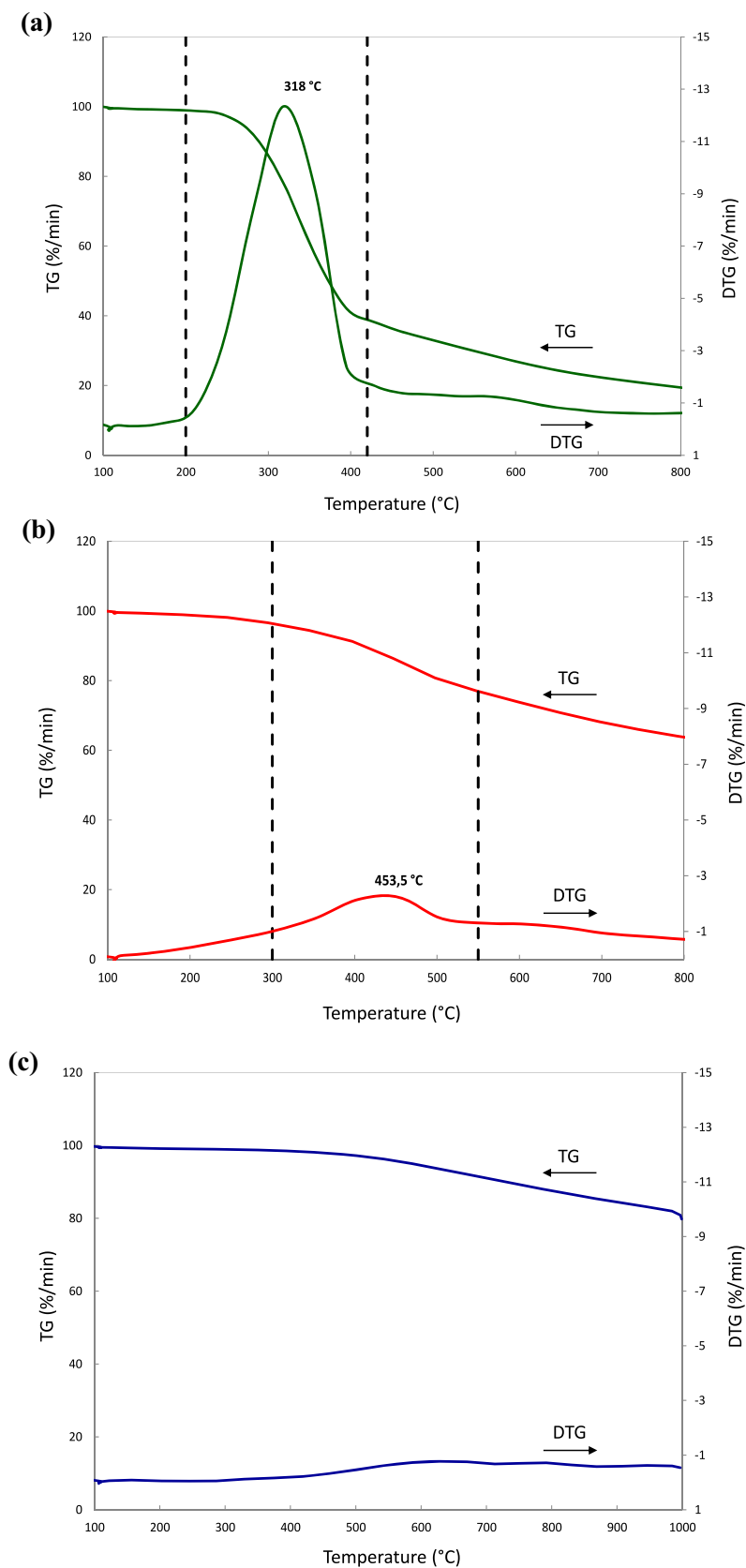


Fig. 2. TG (a) and DTG (b) profiles of different fuels and fuel blends (50% by weight) at 20 °C/min.



**Fig. 3.** Pyrolysis distribution of the TG and DTG curves of (a) wood chip, (b) Sulcis coal and (c) South African coal.

tests. In this case, a SGR of 169.0 kg/m<sup>2</sup> h has been assessed. In any case, with reference to the pilot-scale tests, where the volume of the reactor limits the fuel consumption, a comparison between

coal and biomass gasification should take into account the differences in terms of density (0.2 kg/dm<sup>3</sup> for wood chips and 0.8 kg/dm<sup>3</sup> for both Sulcis and South African coals).



With reference to fuel mixtures, Fig. 2a shows that the experimental TG profile of each blend almost corresponds to that calculated through the arithmetic mean of the profiles of the pure fuels (a maximum gap of about 2–3% has been determined). This indicates that the synergic effects or interactions between the considered coals and wood chips are very slight when they are co-pyrolyzed. With regards to this phenomenon, the technical literature on TGA is quite controversial. While some studies (Lu et al., 2013; Chen and Wu, 2009; Vuthaluru, 2004) indicate that no interactions occur in the fuel blend reactions, several works (Seo et al., 2010; Haykiri-Acma and Yaman, 2010; Zhang et al., 2007) present the opposite result. On the other hand, it is well-known that no interactions occur in pilot- and commercial-scale fixed-bed gasification plants (mainly when the reactor operates at atmospheric pressure).

As reported also by other studies (Lu et al., 2013; Chen et al., 2012; Ceylan and Topçu, 2014), the thermal decomposition process of wood chips can be divided into three stages (see Fig. 3a). The first stage is from the ambient temperature and to about 200 °C, where the loss of both water and light volatiles occurs. The second stage is from the end of the first stage to about 420 °C, where most organic species are decomposed (main pyrolysis process); pyrolytic cracking stage consist of two exothermic simultaneous processes where the main components, hemicelluloses, cellulose and lignin are decomposed and a high amount of volatile matter formation occurs. The third stage is from the end of the second stage to 1000 °C, where the last endothermic decomposition of lignin occurs.

Fig. 3b shows the corresponding results obtained for Sulcis coal. Also in this case, three different stages can be noticed. Fuel decomposition mainly takes place during the second stage, in which a peak of the DTG curve can be observed at a temperature of 453.5 °C. Finally, the thermal decomposition process of South African coal starts at around 450 °C and proceeds at relatively low reaction rate until 1000 °C without any clear demarcations (Fig. 3c).

As for the DTG profile, the peak temperature in biomass curve (318 °C) is lower than other fuels' one, whereas the decomposition intensity (defined as the weight percentage reduction per Celsius degree) is significantly higher. This behavior is mainly due to the structural differences between the considered fuels. In particular, the extension of the peak is related to the volatile content in the

fuel (equal to 73.63% in biomass and 9.09% in South African coal, both by weight). With reference to the coal examined, the decomposition rate strongly depends on the carbon content, which slowly reacts during pyrolysis. This behavior is particularly pronounced for South African coal, characterized by the highest carbon content (74.50% by weight).

Among the fuel blends analyzed in this study, the mixture of wood chips and Sulcis coal (both at 50% by weight) seems the most interesting one, as results from several preliminary tests on pilot-scale gasification plant. When biomass is mixed with Sulcis coal, the pyrolysis behavior assessed by TGA is characterized by four-stage reaction (as shown in Fig. 4) rather than three-stage one observed for the single fuels. The first peak, which occur in the second reaction stage between 200 and 395 °C, can be related to thermal decomposition of biomass in the mixture, while the peak in the third reaction stage between 395 and 510 °C should be a consequence of thermal decomposition of coal. The peak intensity in the third-stage reaction is lower than that of the second-stage one.

### 3.2. Kinetic analysis

As reported above, the decomposition of the considered fuels mainly takes place in the second stage of the overall process, so for kinetics investigation this stage is mainly taken into concern. According to the Flynn–Wall–Ozawa (FWO) model (see Section 2.5), when  $\alpha$  is constant, the values of  $\ln \beta$  versus  $1/T$ , obtained at different values of the heating rate  $\beta$ , can be correlated by a straight line, which slope indicates the apparent activation energy. Fig. 5 shows the linear plot of  $\ln \beta$  versus  $1/T$ , in which slopes give  $E$  at different conversion degrees.

As for wood chips, the analysis considers conversion degrees between 0.2 and 0.8. In the considered range of variation of the conversion degree, the straight lines well represent the process (with a  $r^2$  – the correlation factor – between 0.9904 and 0.9992), and a decreasing activation energy has been obtained. The average activation energy for the pyrolysis process is 116.7 kJ/mol. The literature reports values of the activation energy very different for biomass, due to the non-uniform composition of this kind of fuel. Furthermore, among similar species of biomass, a great difference of pyrolysis kinetics also occurs in certain research (Chen et al., 2012).

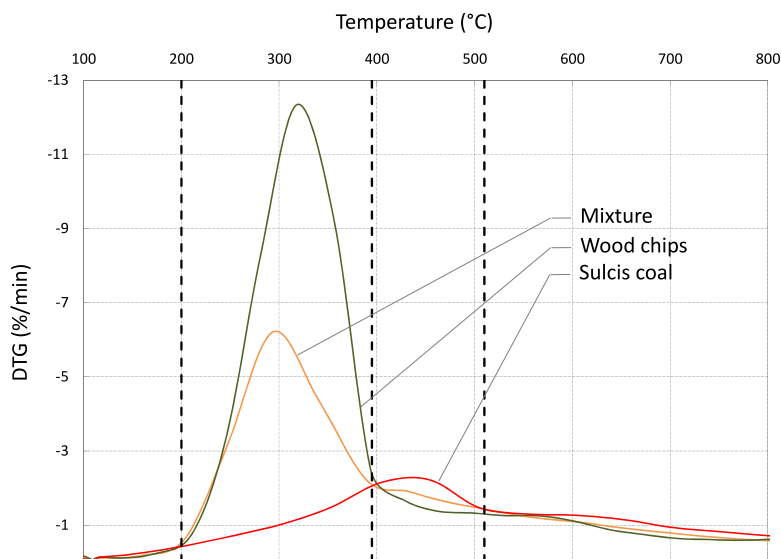
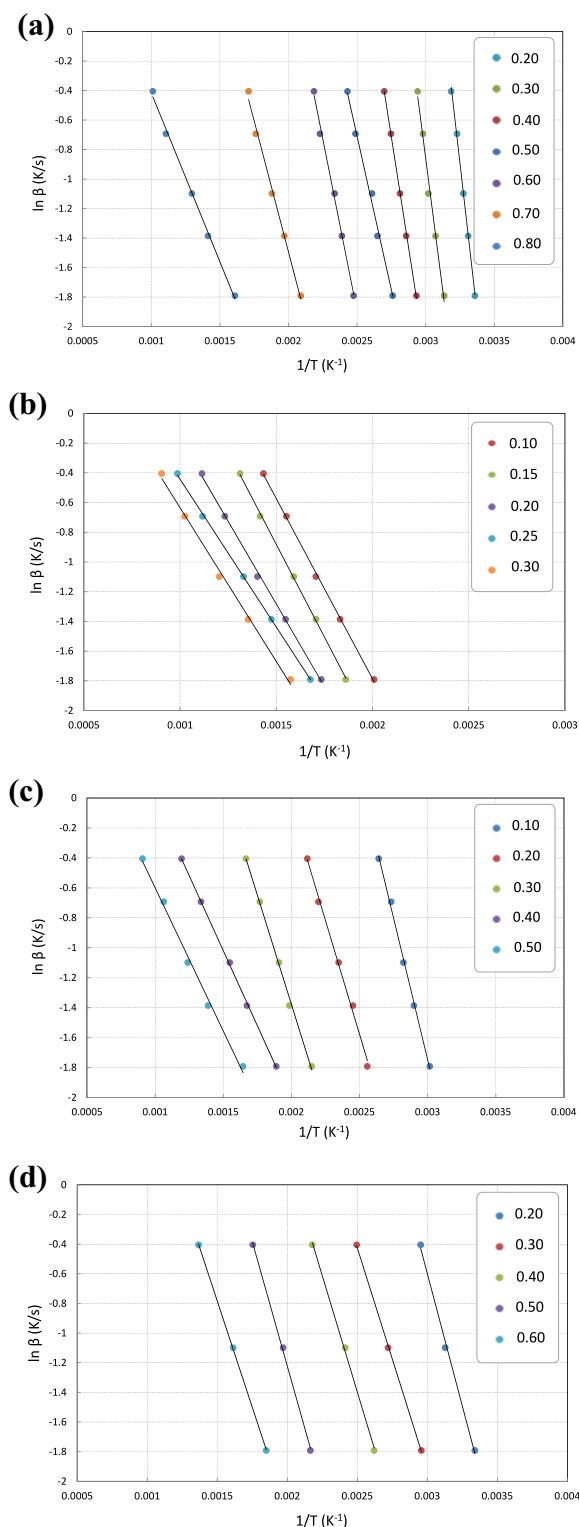


Fig. 4. Comparison of DTG curves for wood chips, Sulcis coal and their mixture.



**Fig. 5.** Determination of activation energy for (a) wood chips, (b) South African coal, (c) Sulcis coal and (d) wood chips and Sulcis coal mixture.

According to that reported by Seo et al. (2011), the activation energy of South African coal samples has been calculated only with a conversion degree between 0.1 and 0.3 (at five different conversion ratios with  $r^2$  between 0.9965 and 0.9996) and the average value of  $E$  is 105.6 kJ/mol (Fig. 5b). This values are relevant to that reported in the previously cited work by Seo et al. (2011), in which an activation energy of 130 kJ/mol has been determined for a

Chinese coal. A conversion degree between 0.1 and 0.5 has been considered for Sulcis coal (Fig. 5c) due to the low correlation values outside this range, and the average value of  $E$  is 113.1 kJ/mol (with  $r^2$  between 0.9947 and 0.9994). For all the samples, different operating conditions have been analyzed in order to avoid heat and mass transfer limitations.

Finally, as for the mixture composed by 50% of wood chips and 50% of Sulcis coal (both by weight), the kinetic analysis has been performed considering an intermediate range of conversion degree (0.2–0.6), due to the low correlation values outside this range (Fig. 5d).

The activation energy strongly depends on the conversion degree; changes in  $E$  value are a consequence of the variation of the reaction mechanism during the pyrolysis process. It means that pyrolysis of a mixture of wood chips and Sulcis coal is a complex process which consists of different reactions. The average activation energy for the second and the third reaction stages are 110.1 and 50.95 kJ/mol, respectively, with  $r^2$  between 0.9971 and 0.9999. The reactivity of biomass is more than that of coal but, as for the second stage reaction, the introduction of biomass only leads to a slight reduction of the activation energy itself. On the other hand, the activation energy in the third stage is more sensitive to biomass content, and the introduction of the biomass in the mixtures involves a decreasing of  $E$ , probably because the thermal decomposition in this stage is dominated by lignin or coal and the activation energy of lignin is relatively low (Lu et al., 2013). In order to have a more accurate assessment of the process behaviors, the analysis of several mixtures with different weight ratios between wood chips and Sulcis coal is currently under investigation and it will be the subject of a future work.

#### 4. Conclusions

TGA of each fuel allows an optimization of the process parameters in the Sotacarbo pilot plant. The considered fuels present very different behaviors: South African coal shows a very low weight reduction and its DTG profile does not present a peak; Sulcis coal is more reactive than South African one and biomass presents a high reduction with a well-defined devolatilization peak. As for fuel blends, the synergic effects between the considered fuels are very slight. The mixture of wood chips and Sulcis coal seems the most interesting one and the pyrolysis behavior is characterized by four-stage reaction.

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